

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(12) UK Patent Application (19) GB (11) 2 309 655 (13) A

(43) Date of A Publication 06.08.1997

(21) Application No 9602203.3

(22) Date of Filing 03.02.1996

(71) Applicant(s)

The Technische Universiteit Delft

(Incorporated in the Netherlands)

134 Julianalaan, Delft, Netherlands

(72) Inventor(s)

Jihad Dakka

Roger A Sheldon

William Ronald Sanderson

(74) Agent and/or Address for Service

T Pearce

Solvay Interlox Limited, PO Box 51,

Patent Department, Moorfield Road, WIDNES,

Cheshire, WA8 0FE, United Kingdom

(51) INT CL⁶

B01J 29/035 , C07D 301/12

(52) UK CL (Edition O)

B1E EAA E1158 E1161 E1191 E1212 E1285 E1382

E1394 E1422 E1432 E1451 E1452 E1701 E1722 E1729

U1S S1519

(56) Documents Cited

US 5364951 A

US 4745221 A

US 4513090 A

US 4465889 A

(58) Field of Search

UK CL (Edition O) B1E

INT CL⁶ B01J 29/04 , C07D 301/12

Online databases: WPI and CLAIMS

(54) Heterogeneous Catalysts

(57) Heterogeneous catalysts comprising one or more metal compounds selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium compounds deposited on the surface of a silicalite are provided. Preferably Sn(IV) and/or Mo(VI) are employed. The catalysts are prepared by reacting a metal halide compound in fluid form with a solid-silicalite.

GB 2 309 655 A

5

10

Heterogeneous Catalysts

This invention concerns heterogeneous catalysts, particularly catalysts for oxidation reactions, and more particularly catalysts comprising metal compounds surface deposited on silicalites.

15 Metal compounds, and especially transition metal compounds have long been known to be active catalysts for chemical reactions. They have often been employed as catalysts for oxidation reactions employing peroxygen oxidants, particularly hydrogen peroxide and alkyl hydroperoxides. In many cases, the catalysts have been employed as homogeneous catalysts, most
20 often either in solution, or forming a soluble reactive species. However, although use of a homogeneous catalysts system may offer advantages in terms of rate of reaction, process economics can often dictate that there is a need for the catalyst to be recovered and/or recycled from the reaction mixture. When a homogeneous catalyst system is employed, this can be a
25 difficult and time consuming operation. This, coupled with increasing regulatory pressures on discharges, particularly of metals, into the environment has led to increasing interest in heterogeneous catalysts, particularly solid catalysts which offer the possibility of relatively simple recovery of catalyst from the reaction medium, eg by filtration. Although it may seem a
30 comparatively simple matter to take a known homogeneous catalyst and chemically support it on a medium that is insoluble under the reaction conditions, the fact that the active species is now immobilised, in a different local environment and in a separate phase from the reagents can considerably reduce its activity, and in extreme cases may prevent the catalytic activity
35 completely.

One heterogeneous catalyst comprising an immobilised metal compound is the well known titanium-silicalite catalyst TS-1 where the titanium is incorporated into the framework of a silicalite, providing a strongly-immobilised

metal. Indeed, TS-1 is a catalyst which is much more effective in heterogeneous form for oxidations by hydrogen peroxide than is Ti(IV) as a homogeneous catalyst, emphasising that homogeneous catalyst activity cannot necessarily be used to predict heterogeneous activity, and vice versa.

- 5 Compounds similar to TS-1 based on certain other silicalites and zeolites are also known. Although active catalysts for certain reactions, the incorporation of a metal catalyst in the framework of a silicalite or zeolite can restrict the range of substrates with which the catalyst can be employed, on account of the restricted access to the metal sites, believed to be caused by the pore size
10 of the silicalite.

One alternative approach to immobilising metal catalysts is to support the catalyst on the surface of an insoluble support. An example of such a surface deposition technique is that taught by Forzatti et al in "Catalysis, Heterogeneous and Homogeneous" ed. B Jannes, pp 509 - 519 (1975) where
15 MoO_3 is deposited onto silica. A further approach is that taught by Inoue et al, Chem. Pharm. Bull. vol 33, pp3583-8 (1985) where MoO_3 and tributyltinchloride were deposited onto charcoal. The catalyst was asserted to be recyclable. Charcoal as a support, however, suffers from the drawback that it can readily absorb organic substrates, rendering them difficult to
20 recover, can catalyse the decomposition of the oxidant, particularly hydroperoxides, and can be gradually oxidised by the oxidant. One other approach is that taught by Kooyman et al, Catalysis Letters vol 13, pp 229 - 238 (1992) where titanium was supported on the surface of silica and silicalite-1. The titanium was supported on the silica and silicalite by reaction
25 between gas phase deposition of TiCl_4 at elevated temperature, and by liquid phase deposition employing a solution of TiCl_4 in heptane. A comparison of the performance in phenol hydroxylation of the surface deposited materials with the above mentioned TS-1 indicated that none of the surface deposited materials had as good an activity as TS-1.

- 30 Notwithstanding the existence of the above-described surface deposited heterogeneous catalysts, it remains desirable to identify additional and/or further such catalysts.

It is an object of the present invention to provide additional or further surface deposited heterogeneous catalysts.

- 35 According to one aspect of the present invention, there is provided a heterogeneous catalyst comprising a metal compound deposited on the surface of a silicalite, characterised in that the metal compound comprises one or more

selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium compounds.

According to a second aspect of the present invention, there is provided a process for the preparation of a heterogeneous catalyst comprising reacting a metal halide compound in fluid form with a solid silicalite, characterised in that the metal halide compound comprises one or more selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium halide or oxyhalide compounds.

The heterogeneous catalysts according to the present invention comprise one or more metal compounds, most commonly metal oxides, selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium compounds, deposited on the surface of a silicalite. Without wishing to be bound by any theory, it is believed that often at least a portion of the surface deposited metal, and preferably at least a significant fraction of the metal compound, for example substantially all of the metal compound, forms a chemical bond to the surface of the silicalite. The weight percent of surface deposited metal compound, expressed as % metal, in the catalyst is often no less than 0.5%, more often no less than 1%, preferably no less than 2% and is often no greater than 25%, more often no greater than 17%. In a number of embodiments, the weight percent of surface deposited metal compound, expressed as % metal, in the catalyst is in the range of from 3% to 6%. The weight percent of surface deposited metal compound in the catalyst can conveniently be measured by the use of surface analysis techniques including particularly energy-dispersive X-ray analysis, often employed in conjunction with scanning electron microscopy. In certain embodiments of the invention, good results have been achieved when 2 compounds of different metals are present, and preferably both tin and molybdenum compounds are surface deposited on a silicalite. When both tin and molybdenum are present, the weight ratio of tin to molybdenum is often in the range of from 10 : 1 to 1 : 10, and preferably from 4 : 1 to 1 : 4.

The metal compounds are often present in the catalysts of the invention in their highest oxidation states, ie Sn(IV), Mo(VI), W(VI), Se(IV) and Zr(IV).

Silicalites that can be employed in the catalysts according to the present invention include substantially aluminium-free silicalites and high Si : Al mole ratio zeolites, particularly silicalite-1, silicalite-2, and those having MCM-41, ZSM-5, ZSM-11, ZSM-12 and ZSM-22 structures. Preferably, the

silicalite is silicalite-1. Other silicalites that may be employed are silicalites in which one or more transition metals are incorporated in the framework of the silicalite, including for example TS-1 and MoS-1. In certain embodiments of the present invention, the mole ratio of Si to Al in the silicalite is often selected to be greater than 75 : 1, and is often less than about 3000 : 1. In many embodiments, the mole ratio of Si to Al is in the range of from 150 : 1 to 2500 : 1. In particular embodiments, and especially when silicalite-1 is employed, good results have been achieved employing a silicalite having a mole ratio of Si to Al of about 1400 : 1.

10 The catalysts according to the present invention are prepared by contacting a metal halide compound selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium halide or oxyhalide compounds in fluid form with a solid silicalite. The metal halide or oxyhalide compounds preferably comprise the metal in its highest oxidation states, ie Sn(IV), Mo(VI), W(VI), Se(IV) and Zr(IV). Metal chlorides and oxychlorides are particularly preferred. Examples of suitable halide or oxyhalide compounds include SnCl_4 , MoCl_6 , MoOCl_4 , MoO_2Cl_2 , WCl_6 , WOCl_4 , SeCl_4 , SeOCl_2 , ZrF_4 and ZrCl_4 .

The silicalite is preferably employed as a calcined, dry solid. The calcination generally serves to remove any organic template remaining from the preparation of the silicalite, and may also activate the silicalite towards reaction with the metal halide or oxyhalide. Calcination is carried out at a temperature above 350°C, often at a temperature of 450°C to 650°C, and often about 500 to 550°C. The calcined silicalite may then be sufficiently dry, particularly for reaction with the metal halide or oxyhalide in gaseous form. For reaction with metal halide or oxyhalide in liquid form, the silicalite is often subsequently dried further, and the further drying is conveniently achieved by heating the silicalite in a hydrocarbon solvent, such as n-heptane, at the solvent's reflux temperature to azeotropically remove further traces of water. After removal of this water, the sample may then be re-calcined to remove traces of the solvent, although this may not be necessary, particularly if the same solvent is to be employed in the subsequent stages of preparation of the catalyst. In many embodiments, when the metal halide or oxyhalide is to be employed in liquid form, following the completion of the removal of water, the silicalite and solvent mixture is employed in the subsequent processing without undergoing further treatment.

The metal halide or oxyhalide can be employed either in liquid form, for example as a solution in a non-aqueous, hydroxyl-free solvent, or in gaseous form. In certain embodiments, when two or more metal halide or oxyhalide compounds are employed, one compound may be employed in liquid form and the other in gaseous form.

When the metal halide or oxyhalide compound is employed as a solution in a solvent, the solvent is non-aqueous and does not comprise hydroxyl groups, on account of the reactivity of water and hydroxyl groups towards the metal halides or oxyhalides. Examples of suitable solvents include nitriles such as acetonitrile, alkanes such as n-pentane and n-heptane, chlorinated solvents such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene, and aromatic hydrocarbons such as toluene and xylene. Mixtures of two or more solvents may be employed if desired, particularly a mixture of acetonitrile and n-heptane. When a mixture of acetonitrile and n-heptane is employed, the volume ratio of acetonitrile to heptane is often in the range of from 0.5 : 1 to 1 : 4. The solution of metal halide or oxyhalide is added with stirring to the silicalite, commonly to the silicalite in the form of a mixture in the same solvent, or one or more of the solvents, as the metal halide or oxyhalide. The addition is normally effected at elevated temperature, commonly at, or within 5°C of, the reflux temperature of the solvent, which is often selected to be from about 70° to 120°C. The addition can take the form of adding one aliquot or a plurality of substantial aliquots of the metal halide or oxyhalide solution, or can be achieved in small increments or continuously over an extended addition time. Commonly, small increments or continuous addition is employed in order to control the rate of emission of any hydrogen halide gases formed in the reaction. Typical addition times are from 3 to 7 hours. On completion of the addition, the mixture is maintained at the elevated temperature until substantially no more hydrogen halide gas is being evolved, often a period of from 5 to 15 hours. The solvent is then separated from the solid catalyst produced, optionally before the reaction mixture has cooled to room temperature, by conventional means, for example decanting the solvent or filtration. The catalyst produced is then washed, usually with several aliquots of water or low molecular weight alcohols, to remove traces of the solvent mixture and unreacted metals, and air dried, often at a temperature > 100°C. The catalyst is then preferably calcined at a temperature above 350°C, often at a temperature of from 450°C to about 500°C to remove traces of solvent that may remain,

commonly for from 15 to 30 hours, depending on the calcination temperature.

When the metal halide or oxyhalide is employed in the gaseous form, the silicalite is employed as a solid. The metal halide or oxyhalide is
5 volatilised using a method appropriate for the particular compound(s) employed. For example, a metal halide or oxyhalide that readily sublimates can be heated to a temperature above its sublimation temperature. Such sublimation may be carried out in the presence of the silicalite, or may be carried out remote from the silicalite with the vaporised metal halide or
10 oxyhalide being transported appropriately into contact with the silicalite. Metal halide or oxyhalide compounds may also be volatilised by passing an inert gas, such as nitrogen or argon through the compound when the compound is in liquid form. This can be achieved at room temperature (about 18 to 25°C) for compounds which are liquid at that temperature, or
15 at an elevated temperature above their melting point for compounds which are solid at room temperature. Preferably, the inert gas is saturated with the metal halide or oxyhalide, and then brought into contact with the silicalite. In certain embodiments, a combination of the sublimation method and the inert gas method can be employed if appropriate, particularly where
20 two different metal halide or oxyhalide compounds are employed.

The contact between the silicalite and the gaseous metal halide or oxyhalide is continued until the desired extent of reaction has occurred. Reaction times may depend on the temperature employed, but are often in the range of from about 1.5 hours to 24 hours. Reaction temperatures
25 employed are often in the range of from 120°C to 400°C. In certain embodiments of the present invention, good results have been achieved employing a reaction temperature of from 140°C to 300°C. It will be recognised that the reaction between the silicalite and the metal halide or oxyhalide in gaseous form is carried out in the substantial absence of air
30 and water to avoid their detrimental effects on the metal halide or oxyhalide.

The weight ratio of silicalite to metal halide or oxyhalide in the process according to the present invention is often selected to be in the range of from 10 : 1 to 1 : 5, and preferably from 5 : 1 to 1 : 2.

35 The catalysts according to the present invention can be employed as catalysts in a wide range of processes. They are suitable for catalysing oxidation reactions, and particularly oxidation reactions employing a peroxygen oxidant. Preferred peroxygen oxidants comprise hydrogen

peroxide and organic hydroperoxides such as t-butyl hydroperoxide. The catalysts are particularly suited to those oxidations for which the heterogeneous catalyst TS-1 can be employed. Examples of processes in which catalysts according to the present invention may be employed

- 5 include oxidation, especially epoxidation, of alkenes; oxidation of amines, hydroxylation of phenols, ammoximation of ketones, oxidation, including hydroxylation, of alkanes, oxidation of alcohols and sulphur oxidations.

The conditions which can be employed for use of the catalysts according to the invention as oxidation catalysts are generally those

- 10 conventional in the art for the oxidation reaction concerned when TS-1 is employed as the heterogeneous catalysis. Mole ratios of oxidant to substrate sub-stoichiometric, stoichiometric or super-stoichiometric for the desired oxidation can be employed as appropriate. For example, a sub-stoichiometric mole ratio may be employed where the substrate is
- 15 particularly reactive, where the desired product is itself susceptible to further oxidation, or comprises more than one functionality sensitive to oxidation, and only partial oxidation is required, whereas a super-stoichiometric mole ratio may be employed where the substrate is deactivated to oxidation.

- 20 The substrate may serve as the only solvent for the oxidation reaction, or additional solvents, usually resistant to oxidation under the prevailing conditions, may be employed. A preferred class of solvents, particularly when hydrogen peroxide is employed as the oxidant, comprises nitriles, particularly acetonitrile and adiponitrile. When organic
- 25 hydroperoxides are employed as oxidant, chlorinated solvents such as dichloromethane and chloroform are commonly employed.

- Elevated temperature, such as from 40°C up to the reflux temperature at atmospheric pressure is commonly employed. Temperatures above the reflux temperature at atmospheric temperature can be employed
- 30 by using elevated pressure, such as by carrying out the reaction in an autoclave.

- It will be recognised that the amount of catalyst employed in reaction mixtures can vary depending on, for example, the nature of the reaction being catalysed, the reaction conditions employed, and particularly on the
- 35 weight percent of surface deposited metal compound in the catalyst. Generally, a smaller amount of a catalyst having a higher weight percent of surface deposited metal compound would be employed compared with one with a lower amount of metal compound, all other things being equal. The

catalyst according to the present invention is typically present in the reaction mixture at a concentration of greater than 1 g/l, often greater than 2.5 g/l, and preferably greater than 5 g/l. A catalyst concentration of less than 50 g/l, and often less than 25 g/l is usually employed. In certain
 5 embodiments of the present invention, a catalyst concentration in the range of from 7.5 g/l to 15 g/l is employed.

One oxidation for which the catalysts are especially suitable is the oxidation of alkenes. Examples of alkenes that can be contemplated for oxidation by the catalysts according to the present invention include
 10 propylene, but-1-ene, but-2-ene, isobutene, butadiene, the pentenes and notably isoamylene, piperylene, the 1-, 2- and 3-hexenes, the hexadienes, hept-1-ene, 3-ethylpent-2-ene, oct-1-ene, diisobutylene, 2,4,4-trimethyl pent-1-ene and -2-ene, non-1-ene, dec-1-ene, undec-1-ene, dodec-1-ene, tridec-1-ene, tetradec-1-ene, pentadec-1-ene, hexadec-1-ene, heptadec-1-
 15 ene, octadec-1-ene, nonadec-1-ene, eicos-1-ene, the trimers and tetramers of propylene, the polybutadienes, isoprene and the terpenes such as the terpinenes, limonene, terpinolene, sabinene, pinene, camphene, myrcene, cadinene, phellandrene, caryophyllene, Δ -3-carene, cedrene, santalene, calarene, colophene and the polyterpenes as well as their derivatives such
 20 as geraniol, nerol, linalol and linalyl acetate, methylenecyclopropane, cyclopentene, cyclopentadiene, cyclohexene, methylenecyclopentane, methylenecyclohexane, norbornene, cycloheptene, vinylcyclohexane, vinylcyclohexene, styrene, 4-chlorostyrene, cyclooctene, the cyclooctadienes, vinylnorbornene, indene, tetrahydroindene, alpha-
 25 methylstyrene, dicyclopentadiene, divinylbenzene, cyclododecene, cyclododecatriene, diphenylbutadiene, vitamin A, beta-carotene, vinylidene fluoride, allyl chloride and bromide, the trichloropropylenes, crotyl chloride, methallyl chloride, the dichlorobutenes, allyl alcohol, methallyl alcohol, but-2-ene-ol, but-2-ene diol, the cyclopentene diols, 4-pentenol, 2-methylpent-
 30 2-ene-1-ol, 1,2-dihydroxy-4-vinylbenzene, 2,7-octadien-1-ol, cyclohexenylcarbinol, tridec-2-ene-1-ol, the unsaturated steroids, ethoxyethylene, eugenol, isoeugenol, anethole, safrole, isosafrole, the unsaturated carboxylic acids of all types such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, vinylacetic acid and the unsaturated fatty
 35 acids including more particularly oleic, linoleic, palmitoleic, linolenic, vaccenic, gadoleic, ricinoleic and eleostearic acids and the natural fats and oils which contain them as well as the esters of these unsaturated acids such as the alkyl acrylates and methacrylates, diallyl maleate, methyl-7-

hydroxy-5-heptenoate, methyl oleate and the esters of unsaturated alcohols such as allyl carbonate and allyl acetate. Additional aromatic alkenes that may be oxidised by the catalysts according to the present invention include diallyl phthalate, diallylisophthalate, diallylethers of bis-phenol A and H,
5 stilbenes and substituted stilbenes.

When hydrogen peroxide is employed as oxidant for the oxidation of an alkene in the presence of a catalyst according to the present invention, a low molecular weight nitrile solvent, preferably acetonitrile, is often employed to favour preferential formation of epoxides. Use of a low
10 molecular weight alcohol, such as methanol, as solvent often favours preferential formation of non-epoxide oxidation products such as monoethers, formed by ring-opening of the epoxide. When t-butylhydroperoxide is employed, a low molecular weight chlorinated solvent, such as dichloromethane is often employed.

15 The heterogeneous catalysts according to the present invention can often readily be recycled by simply separating the catalyst from the reaction medium by use of an appropriate technique, such as filtration. Commonly, prior to re-use of such a recycled catalyst, the catalyst is dried, often in air and under elevated temperature, such as up to 150°C.

20 Having described the invention in general terms, specific embodiments thereof are described in greater detail by way of example only.

Example 1.

25 3.5 g of silicalite-1 having a Si : Al mole ratio of 1400 : 1 was calcined in air at 550°C for one night, and then refluxed in a reactor in 400ml n-heptane for 16 hours until all water present had been azeotropically removed. After cooling to room temperature, a solution of 1g SnCl₄ in 10 ml acetonitrile and 30ml n-heptane was added dropwise to the reactor over 2 hours with stirring
30 at reflux and stirred at reflux over 1 night, until no more HCl was evolved. The reaction mixture was allowed to cool to room temperature, the solid catalyst separated from the solvent, washed with water, dried in air at 120°C, and then calcined in air at 500°C for 20 hours. The product obtained was analysed by Inductively-coupled Plasma spectrometry following dissolution in a
35 1:1 vol: vol mixture of concentrated HF and Sulphuric acid. The product was found to comprise 11.4% w/w Sn.

Example 2

The method of Example 1 was followed, except that 1.5g MoOCl_4 was employed in place of the SnCl_4 . The product obtained comprised 7.8% w/w Mo.

5

Example 3

The method of Example 1 was followed, except that 1.5g SeOCl_2 was employed in place of the SnCl_4 . The product obtained comprised 10.5% w/w Se.

10

Example 4

The method of Example 1 was followed, except that 1.5g ZrF_4 was employed in place of the SnCl_4 . The product obtained comprised 4.3% w/w Zr.

15 Example 5

The method of Example 1 was followed, except that a solution of 1.5g SnCl_4 and 0.5g MoOCl_4 in 50ml acetonitrile and 50ml n-heptane was added dropwise over 5 hours at reflux temperature, in place of the SnCl_4 solution. The product obtained comprised 6.9% w/w Sn and 4.3% w/w Mo.

20

Example 6

2.5g of silicalite-1 having a Si : Al weight ratio of 1400 : 1 was dried by heating at 1°C per minute to 500°C in a flow of air, and maintained at 500°C for 1 night. The dried silicalite was then mixed with 1g MoOCl_4 at room temperature under argon, and poured into a tube reactor. A stream of dry nitrogen was saturated at room temperature with 3g SnCl_4 . The saturated nitrogen was then circulated over the mixture of silicalite and MoOCl_4 at 150°C for 1 night, and then allowed to cool to room temperature. The solid obtained was washed with distilled water, air dried and calcined at 550°C for 20 hours. The product obtained comprised 6.7% w/w Sn and 11.3% w/w Mo.

30

Example 7

The method of Example 6 was followed, except that the saturated nitrogen was circulated over the mixture of silicalite and MoOCl_4 at 280°C. The product obtained comprised 1.4% w/w Sn and 10.5% w/w Mo.

35

Example 8

100mmol of 1-hexene, 25 mmol H_2O_2 (as a 35% w/w aqueous solution), 0.25g of the catalyst of Example 1 and 15ml of acetonitrile were heated at 100°C in an autoclave for 5 hours. The reaction mixture was then allowed to cool to room temperature. Calculated on the basis of the moles of H_2O_2 originally present, 68% of 1-hexene was converted, yielding 44% epoxide, a selectivity to epoxide of 65%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 32%.

10 Example 9

The method of Example 8 was repeated, except that the catalyst of Example 2 was employed. Calculated on the basis of the amount of H_2O_2 originally present, 38% of 1-hexene was converted, yielding 27% epoxide, a selectivity to epoxide of 74%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 27%.

Example 10

The method of Example 8 was repeated, except that the catalyst of Example 3 was employed. Calculated on the basis of the amount of H_2O_2 originally present, 32% of 1-hexene was converted, yielding 21% epoxide, a selectivity to epoxide of 65%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 32%.

Example 11

25 The method of Example 8 was repeated, except that the catalyst of Example 4 was employed. Calculated on the basis of the amount of H_2O_2 originally present, 40% of 1-hexene was converted, yielding 20% epoxide, a selectivity to epoxide of 50%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 50%.

30

Example 12

The method of Example 8 was repeated, except that the catalyst of Example 5 was employed. Calculated on the basis of the amount of H_2O_2 originally present, 68% of 1-hexene was converted, yielding 58% epoxide, a selectivity to epoxide of 85%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 14%.

35

Example 13

The method of Example 12 was repeated, except that 0.4g of the catalyst of Example 5 was employed. Calculated on the basis of the amount of H_2O_2 originally present, 80% of 1-hexene was converted, yielding 68% epoxide, a selectivity to epoxide of 85%, and giving a selectivity to other oxygenated products (eg 2-hexanone) of 13%.

Example 14

The method of Example 12 was repeated, except that 100 mmol of 1-octene was employed. Calculated on the basis of the amount of H_2O_2 originally present, 64% of 1-octene was converted, yielding 56% epoxide, a selectivity to epoxide of 88%, and giving a selectivity to other oxygenated products of 1.2%.

Examples 15 to 20

In Example 15, the method of Example 12 was repeated. In Example 16, the method of Example 12 was repeated except that methanol was employed in place of the acetonitrile. In Examples 17 and 18, the methods of Examples 15 and 16 respectively were followed, except that the catalyst of Example 4 was employed. In Examples 19 and 20, the methods of Example 15 and 16 respectively were followed, except that the catalyst of Example 3 was employed. The results, calculated on the basis of the moles of H_2O_2 originally present, are given in Table 1 below.

Table 1.

Example	Substrate Conversion (%)	Epoxide Yield (%)	Selectivity to Epoxide (%)	Selectivity to Other Oxidation Products
15	90	76.5	85	13
16	88	1.7	2	95
17	40	20	50	49
18	24	9	36	60
19	32	2	7	85
20	32	3.2	10	87

Example 21

30mmol of allyl chloride, 6 mmol H_2O_2 (as a 35% w/w aqueous solution), 0.25g of the catalyst of Example 5, and 30ml of acetonitrile were heated at

90°C in an autoclave for 2 hours. The reaction mixture was then allowed to cool to room temperature. Calculated on the basis of the amount of H₂O₂ originally present, 5% of allyl chloride was converted, yielding 3% epoxide, a selectivity to epoxide of 60%.

5

Example 22

10mmol of cyclohexylamine, 10 mmol H₂O₂ (as a 35% w/w aqueous solution), 0.2g of the catalyst of Example 5, and 5ml of t-butanol were heated at 80°C in an autoclave for 5 hours. The reaction mixture was then allowed to cool to room temperature. Calculated on the basis of the amount of H₂O₂ originally present, 10% of cyclohexylamine was converted, yielding 10% oxime, a selectivity to oxime of 100%.

Claims

1. A heterogeneous catalyst comprising a metal compound deposited on the surface of a silicalite, characterised in that the metal compound comprises one or more selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium compounds.
2. A process for the preparation of a heterogeneous catalyst comprising reacting a metal halide compound in fluid form with a solid silicalite, characterised in that the metal halide compound comprises one or more selected from the group consisting of tin, molybdenum, tungsten, zirconium and selenium halide or oxyhalide compounds.
3. A catalyst or process according to either preceding claim, characterised in that the metal compound(s) are selected from Sn(IV) and Mo(VI) compounds.
4. A catalyst or process according to any preceding claim, characterised in that the silicalite is silicalite-1.
5. A catalyst or process according to any preceding claim, characterised in that the weight ratio of Si to Al is in the range of from 150 : 1 to 2500 : 1, and is preferably about 1400 : 1.
6. A catalyst or process according to any preceding claim, characterised in that both Sn(IV) and molybdenum(VI) are present.
7. A catalyst or process according to claim 6, characterised in that the weight ratio of tin to molybdenum is often in the range of from 10 : 1 to 1 : 10, and preferably from 4 : 1 to 1 : 4.
8. A catalyst or process according to any preceding claim, characterised in that the silicalite has been calcined at a temperature above 350°C, and preferably at a temperature of 450°C to 650°C.
9. A process according to any one of claims 2 to 8, characterised in that the metal halide or oxyhalide is employed in liquid form.

10. A process according to claim 9, characterised in that a solution of metal compound(s) in a mixture of acetonitrile and n-heptane is employed, the volume ratio of acetonitrile to heptane preferably being in the range of from 0.5 : 1 to 1 : 4.
11. A process according to any one of claims 2 to 8, characterised in that the metal halide or oxyhalide is employed in gaseous form.
12. A process according to claim 11, characterised in that a reaction temperature of from 140°C to 300°C for the reaction between the metal halide compound and the solid silicalite.
13. Use of a catalyst according to any one of claims 1 and 3 to 8, or obtained by a process according to any one of claims 2 to 12, as a catalyst for an oxidation reaction.
14. Use according to claim 13, characterised in that the oxidation process is epoxidation of an alkene with a peroxygen oxidant.
15. Use according to claim 13 or 14, characterised in that the oxidant is hydrogen peroxide or t-butylhydroperoxide.



Application No: GB 9602203.3
Claims searched: 1-15

Examiner: John Warren
Date of search: 16 April 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B1E

Int Cl (Ed.6): B01J 29/04; C07D 301/12

Other: Online databases: WPI and CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 5 364 951 ENIRICHERCHE - see Claim 2	1
X	US 4 745 221 MONTEDIPE - see Example 5	1
X	US 4 513 090 EXXON - see Catalyst E, Claims 5 and 9	1
X	US 4 465 889 SUMMIT - see Example 15	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

THIS PAGE BLANK (USPTO)